

MODIFIED ALUMINOSILICATE CATALYSTS BASED ON CENOSPHERES OF POWER PLANTS FOR PROCESSING FUEL OIL INTO LIGHT FRACTIONS

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ABSTRACT

In this work the narrow fractions of non-perforated cenospheres from the combustion of Ekibastuz coal at the Almaty TPP-2 with an aluminosilicate module $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$ and an iron content of 3.03-3.67 wt. % in Fe_2O_3 have been researched. It was shown that the composite containing of activated zeolite based on Almaty TPP-2 cenospheres is optimal for obtaining of light gas oil during cracking in both inert medium and trace air quantity. The composite also showed maximum activity during oxidative cracking of vacuum distillate of Zhetybay oil (Kazakhstan). In the presence of the developed catalysts, the symmetric decomposition of the high-molecular-weight hydrocarbons contained in fuel oil was with the formation of alkenes and alkanes of the relative homologous series, starting from heptene-1 and heptane ending with octadecen-1 and octadecane. As a result of the study, an innovative method of oxidative cracking of fuel oil in the presence of cheap catalysts, synthesized on the basis of natural zeolites of Kazakhstan deposits and zeolites obtained from fly ash from thermal power plants has been developed.

KEYWORDS: Cracking, Fuel Oil, Cenospheres, Natural Zeolite & Fly Ash from TPP

Received: May 16, 2019; **Accepted:** Jun 06, 2019; **Published:** Jul 16, 2019; **Paper Id.:** IJMPERDAUG2019111

INTRODUCTION

The lack of proven reserves and production of light petroleum products in recent decades has led to an intensification of the search for new approaches to the processing of residual high-boiling fractions (Liu et al, 2004; Prabhaharet al, 2018; Pandey, 2018). Using only 10% of oil residues, which are still used as boiler fuel, is equivalent to producing 50-60 million tons of oil per year. Fuel oil contained in heavy oils is up to 50% and higher, and much of it is used to produce boiler fuel or raw materials for the production of bitumen and coke, which is the main reserve for the deepening of oil refining (Pandey, 2018; Abul-Hamayel, 2002; Guerzonian and Abbot, 1993). The main obstacle to the processing of fuel oil in catalytic cracking (FCC) units is the increased coking ability of the raw materials and the high content of metals, mainly nickel and vanadium. The need to create low-cost technologies for the processing of heavy raw materials in the industry of Kazakhstan has increased the urgency of finding new methods and developing efficient catalytic systems based on local raw materials (Tashmukhambetova et al., 2017; Tulepov et al., 2019; Kairbekov et al., 2015). The word “cenosphere” is named on the basis of the

Greek words “kenos” – “hollow” and “sphaera” – “sphere”. Energy ash cenospheres are a promising object for single-stage production of microspherical zeolites combining a zeolite structure of this type with the spherical shape of the original cenospheres preserved. At the same time, the material of the cenospheres performs a dual function - a forming matrix and a source of Si and Al, which are necessary for building the skeleton of a zeolite. The mineral-phase composition of the cenosphere, determined by X-ray phase analysis, refers to a glass-ceramic material based on aluminosilicate glass (Vereshchagina et al., 2004; Anshits et al., 2001; Zinoviev et al., 2016; Fomenko et al., 1998; Rubio and Izquierdo, 2010; Yemelyanova et al., 2015).

The aim of the work was to develop technology for processing fuel oil into light oil fraction on the activated zeolite based on Almaty TPP-2 cenospheres.

EXPERIMENTAL

In this research, products of various cenosphere concentrate fractionation stage sequence of Almaty TPP-2 are used to analyze the chemical composition of close-cut globule fractions. The chemical composition of the activated zeolite-containing composite was determined by X-ray spectral fluorescent method. Narrow fractions of non-perforated cenospheres from the combustion of coal of Ekibastuz field (Kazakhstan) at the Almaty Thermal Power Plant-2 (Kazakhstan) with an aluminosilicate module $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$ and an iron content of 3.03-3.67 wt. % in Fe_2O_3 (Table 1) were used.

Table 1: Chemical and Phase Composition of Narrow Fractions of Cenospheres

Sample	Fraction, mm	Macrocomponent Composition, wt. %			$\text{SiO}_2/\text{Al}_2\text{O}_3$, wt %	Crystalline Phase, wt. %			Glass Phase	S_{BET} , m^2/g
		SiO_2	Al_2O_3	Fe_2O_3		Quartz	Mullite	Calcite		
T-3.2	-0.18+0.08	67.60	20.95	3.03	3.2	3.4	0.8	0.5	95.4	125
H-3.2	-0.18+0.08	66.50	20.71	3.67	3.2	n.d.*	n.d.*	n.d.*	n.d.*	125

*n.d. – not determined

This composition of the cenospheres is preferable for the crystallization of zeolite NaP with a gismondine type framework (Itoh et al., 1984; Rigutto et al., 2007; Sadeghbeigi, 2000). The chemical composition of the activated zeolite-containing composite was defined by X-ray spectral fluorescent method. A phase composition of the zeolite-containing composites was identified by X-ray spectral method. The measurements were performed on X-ray diffractometer DRON-4, equipped with a controlling micro ECM “Iskra-330” with a relative error was 10%. X-ray diffraction patterns and X-ray diffraction patterns of clean compounds included in the composition of the analyzed samples were interpreted using a card file “ASTM Powder Diffraction File”.

The value of the catalyst surface area was measured by a heat desorption method that enables to measure the surface within the range of 0.1-500 m^2/g . IR spectroscopy of the catalysts was carried out on Specord IR-75 of Karl Zeiss brand. Catalyst powders were pressed in with KBr (100 mg KBr and 1 mg of sample). Acid sites of the catalyst surfaces were defined by IR-spectroscopy on ammonia and carbonous oxide (II) adsorption. A thermal test of the catalysts was carried out on a derivatograph Q-1500D (MOM, Hungary). The temperature variation range during the tests was from 20 up to 1,000°C at the heating rate of 10°/min. The methodology of the experiment has been developed previously in the laboratory (Ibrasheva and Zhubanov, 2000; Ibrasheva et al. 2001; Zaripova et al. 2015). The content of each fraction was measured by a gravimetric method and presented in % wt. The content of sulfur in fuels and vacuum gas oils was measured by a high-temperature sample oxidation method with following acid-base titration of the resulting sulfuric acid.

The content of oxygen-and sulfur-containing compounds in the starting original fuels and gasoline and kerosine-gasoil fractions obtained in the result of cracking was measured by IR-spectroscopy. It enables to define a qualitative composition of hydrocarbons in the analyzed samples.

When performing oxidative catalytic cracking, the suspension of the specific catalyst composition with a cracking agent was supplied into the flow-type silica reactor at the specific temperature and constant mixing with inert gas. Vapors coming out of the reactor were condensed in the fridge, the liquid products of cracking were collected in an ice-cooling Wurtz flask, and gaseous products – in a gas meter. During cracking, the balance of gaseous hydrocarbons isolation rate and their supply into the gas-meter was measured by a mercury pressure gauge. After the experiment completed, a yield of gaseous, liquid fractions and coke (% wt.) was analyzed. Gaseous product weight was defined on gas density and liquid fraction weight – by weighting the Wurtz flask on the analytical scales before and after the experiment. Then the liquid fraction was distilled, resulting in measuring gasoline, light gas oil and heavy residue content in cracking products. Coke formation was analyzed on the results of reactor weighting before and after catalytic cracking performance. Cracking gaseous products were analyzed on a gas chromatograph with a flame-ionization detector on a column: for hydrocarbon gases-2 m long and 2 mm inner diameter (a sorbing agent Porapak with the particles of 8.2-8.3 mm). Non-hydrocarbon gases were analyzed by using a packed column of 1 m long, filled with zeolite NaX with the particles of 0.25-0.5 mm. An individual composition of kerosine-gasoil fractions was defined by using a chromatomass-spectrometer HP 5890/5972. A capillary column SPB-5 (Supelco) 30 cm long, with inner diameter of 0.25 mm and filter coating thickness of 0.25 μm was used. The detector was used in SCAN-mode. For magnetic measurements, a vibration magnetometer AMH-500 Hysteresisograph (Italy) was used, and electron microscopic studies and electron probe analysis were performed using the Camebax-Microbeam instrument (France). The phase composition was monitored by X-ray analysis using the Dron-0.5 X-ray diffractometer, the chemical composition of the catalyst surface was studied using the ES-2401 X-ray photoelectron spectrometer, and the chemical composition of the surface was studied using the Auger spectrometer pH1-590.

RESULTS AND DISCUSSIONS

The IR-spectrum of the aluminosilicate catalyst is presented in the Figure 1. The intensive strip of absorption in the range of the frequencies of 1,200-1,000 cm^{-1} is observed. This interval of frequencies is characteristic for the groups Si-O, Al-O, Si-O-Al: ν 1,100, 1,066, 1,022, 1,050, 900 cm^{-1} . Absorption strips in low-frequency area of a spectrum from 668 to 614 cm^{-1} belong to Fe-O in the Fe_2O_3 group. The EPR method is successfully applied to a research of forms and a condition of the iron, as a part of glasses (magneto-ordered phases and solid solutions with participation of Fe^{3+} cations) (Yemelyanova et al., 2013; Hamasaki et al., 2008; O'Connor, 2007). In connection with this, the electronic magnetic resonance was used as one of methods of definition of iron conditions in cenospheres. The narrow line with a g-factor 4.3 and also the wide line, which is superposition of two symmetric signals with g-factors 2.20-2.06 (I) and 2.2-2.3 (II) are observed in a typical spectrum of the EPR of cenospheres.

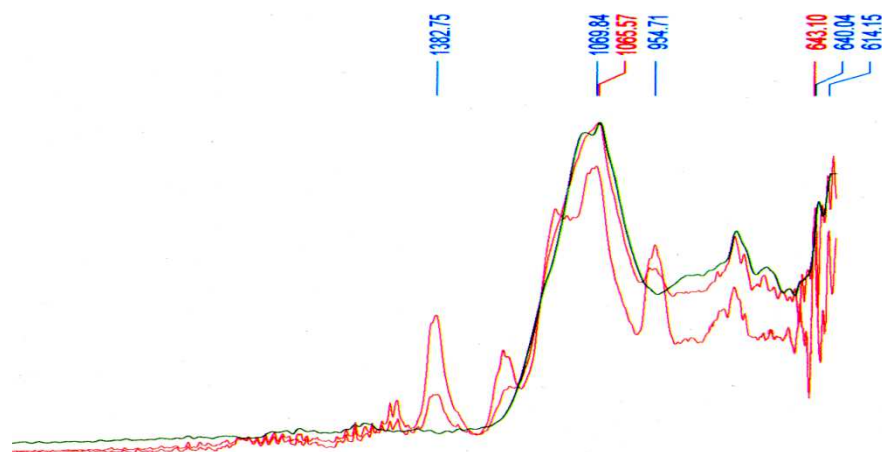


Figure 1: IR-Spectrum of the Microspherical Aluminosilicates Excreted from Ash of the TPP-2 of Almaty (Kazakhstan)

In this work, the narrow fractions of non-perforated cenospheres from the combustion of Ekibastuz coal at the Almaty TPP-2 with an aluminosilicate module $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.2$ and an iron content of 3.03-3.67 wt. % in Fe_2O_3 (Table 1) have been researched. Such a composition of the cenospheres is preferable for the crystallization of zeolite NaP with a gismondine type framework (Itoh et al., 1984; Rigutto et al., 2007; Sadeghbeigi, 2000).

In this work, depending on the conditions, the transformation of the main mass of the cenospheres lasts from 24 to 72 hours, while the degree of transformation to zeolite was very high and reached 96%. The peculiarities of the chemical and mineral-phase composition of the cenospheres, combined with their microspheric design, the presence of an internal cavity, high strength, thermal stability and chemical resistance, make it possible to obtain on their basis microspheric catalysts of fuel cracking (Omarova et al., 2019; Tuktin et al., 2019; Sassykova et al., 2019; Aubakirov et al., 2017). In this study, it was shown, that the composition and the structure of the glass-crystalline material of the cenospheres is an organized (corpuscular) structure of porous composites from the cenospheres, which has good surface wettability with aqueous solutions of salts of both the cenospheres themselves and the porous glass-crystalline material on their basis. It is proved by a degree of a limiting angle of glass watering, which is $55-82^\circ$ depending on a treatment class for the contact surfaces.

A complex of the physical-chemical methods used demonstrated that cracking activity of the optimal catalysts is determined by forming in their composition from 20 up to 30 % of wide-pore zeolite-like crystalline T-type structures containing TO_4 -group of zeolitic framework, which intensify acidity of the active centers. A structure of the generated crystalline phases depends on a mineral composition, a ratio of the components and the composite catalysts activation conditions. The composite containing of activated zeolite based on Almaty TPP-2 cenospheres is optimal, in terms of light gas oil yield during cracking in both inert medium and trace air quantity. It should be mentioned that the composite developed also showed maximum activity during oxidative cracking of vacuum distillate of Zhetybay oil (Kazakhstan).

For the processing of hydrocarbon raw materials by catalytic cracking, it is effective to apply preliminary electromagnetic excitation of hydrocarbon molecules. In this case, the already excited hydrocarbon molecules can interact with the active tetrahedra ensemble of zeolite-alumino silicate catalysts, which increases the efficiency of the catalytic cracking process, especially of oil residues. Apparently, the effect of wave action on petroleum and its products by means of high-frequency electromagnetic field (Kasaikina et al., 2014) is associated with the presence of magnetic particles in the

composition of oil (Hamasaki et al., 2008; O'Connor, 2007; Omarova et al., 2019; Tuktin et al., 2019; Sassykova et al., 2019; Aubakirov et al., 2017; Kasaikina et al., 2014; Tanimoto et al., 1998), and the action of the electromagnetic field is to destroy aggregates of colloidal magnetic particles and activate their surface due to heating. The conducted studies show that the multifunctional, self-adjusting catalyst of oxidative cracking of organic substances considered in the work can be successfully used for oil and oil products, in order to reduce their density, reduce viscosity and obtain light carbon fractions. The initiators of the process, which, as a rule, lead to the cracking of high-molecular fractions, are singlet oxygen and OH, OOH free radicals.

Table 2 presents the results obtained when cracking M-100 fuel on the activated zeolite gained, on the basis of Almaty TPP-2 cenospheres and their composites in the inert medium and the presence of air additions in the reactor.

In the presence of the developed catalysts, the symmetric decomposition of the high-molecular-weight hydrocarbons contained in fuel oil occurred with the formation of alkenes and alkanes of the relative homologous series, starting from heptene-1 and heptane and ending with octadecen-1 and octadecane. The conditions of cracking produce a sufficient effect on destruction of various hydrocarbon fuel fractions (Tashmukhambetova et al., 2017; Amghizar et al., 2017; Baiseitov et al., 2017).

Table 2: Cracking of M-100 Fuel Based on a Zeolite-Containing Composite

Zeolite Content in Composite, % wt.	Cracking Product Yield, % wt.							Total
	Gas	Gasoline	Light Gas Oil 185-340°C	Light Gas Oil 340-350°C	$\Sigma_{\text{light gas oil}}$	Heavy Residue	Losses	
In the Inert Medium								
0	2.0	1.7	14.8	11.4	26.2	71.0	0	100.9
5	1.6	1.8	30.4	19.6	50.0	46.8	0	100.2
10	1.1	1.2	37.8	16.0	53.8	42.8	1.1	100.0
14	1.4	0.9	51.6	19.8	71.4	27.1	0	100.8
20	0.9	0.8	32.3	11.1	43.4	55.2	0	100.3
50	1.3	0.9	28.7	8.8	37.5	59.9	0.4	100.0
80	0.9	0.9	25.2	5.3	30.5	67.6	0.1	100.0
100	0.8	0.8	20.3	3.1	23.4	73.9	1.1	100.0
When Supplying Air ($\omega = 0.15 \text{ h}^{-1}$)								
0	2.8	2.0	21.7	12.2	33.9	62.2	0	100.9
5	1.9	1.2	32.6	16.2	48.8	48.4	0	100.3
10	0.9	0.9	47.6	13.3	60.9	37.5	0	100.2
13	1.2	1.1	48.4	28.8	77.2	20.3	0.2	100.0
14	0.8	1.1	52.5	33.2	85.7	11.9	0.5	100.0
15	1.1	1.1	46.2	21.6	67.8	29.9	0.1	100.0
20	1.3	1.3	37.9	16.2	54.1	42.7	0.6	100.0
50	1.3	1.1	33.7	9.9	43.6	53.5	0.5	100.0
80	1.4	1.0	28.6	7.9	36.5	60.8	0.3	100.0
100	1.1	0.9	26.1	5.9	32.0	65.6	0.4	100.0
Composition contains: $\text{SiO}_2 - 67 \text{ wt.}\%$, $\text{Al}_2\text{O}_3 - 20.95 \text{ wt.}\%$, $\text{Fe}_3\text{O}_4 - 3.03 \text{ wt.}\%$; specific surface area – 125 m^2/g , bulk density – 0.75 g/cm^3 ($\omega_{\text{susp.}} = 1.0 \text{ h}^{-1}$, $T = 470 \text{ }^\circ\text{C}$). Pre-wave treatment of fuel oil: frequency – 57-65 MHz, power – 0.2-1.0 kW, temperature – 50 $^\circ\text{C}$, processing time – 3 hour.								

During thermal cracking in the inert atmosphere and in the air presence, the lightest hydrocarbons are not formed, as evidenced by the fact that in the resulting gas oils, alkenes and alkanes with a number of carbon atoms in the chain equal to nine and more were revealed. It was found that the macrocomponent chemical composition of the obtained narrow

fractions of non-perforated cenospheres is presented in the form of pair dependences of the $\text{Al}_2\text{O}_3/\text{Fe}_2\text{O}_3$ content. The obtained dependences of the Al_2O_3 content on the concentration of the Fe_2O_3 fractions of cenospheres of a certain size allow to distinguish two sets of compositions, for which the coefficients in the regression equation almost coincide. The first includes the cenospheres of the $-0.18 + 0.08$ mm fraction, isolated from concentrates. The second includes a fraction of $-0.5+0.25$ mm and a fraction of $-0.2 + 0.16$ mm cenospheres of low bulk density ($0.3\text{-}0.32$ g/cm³).

CONCLUSIONS

- The catalysts on the base of cenospheres of TTP-2 (Almaty, Kazakhstan) for preparing cracking catalyst has been synthesized. Innovative technology for processing fuel oil into light oil fraction on the activated zeolite based on Almaty TPP-2 cenospheres has been developed.
- Density-based cenosphere concentrate hydrodynamic fractionation modes are worked-out, and lab-scale batches of cenosphere close-cut fractions are developed at the lab-scale unit.
- A complex of physicochemical methods (X-ray, X-ray fluorescent, derivatographic, IR spectrometry, BET, EPR) found that the cracking activity of optimal catalysts is determined by the formation in their composition from 20 to 30% of wide T-type zeolite-like crystalline structures containing the TO_4 group of zeolite frame, which increase the acidity of the active centers. The structure of the resulting crystalline phases depends on the mineral composition, the ratio of components and the activation conditions of the composite catalysts. X-ray phase analysis showed that this is due to the formation of a coarse crystalline structure in optimal catalysts at the stage of their calcination, while inactive ones remain X-ray amorphous. It was shown that crystalline zeolite-like structures of different mineral composition are responsible for the catalytic activity during the cracking of fuel oil differing in their hydrocarbon composition.
- The activation process affects the change in the values of the specific surfaces of the catalysts after calcination. For catalytically active composites, they decrease by 2.0-3.5 times, and for inactive ones - by 22-29%.

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